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(54) PASTE TYPE NICKEL ELECTRODE FOR ALKALINE STORAGE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a paste type nickel electrode for an alkaline storage battery, in which high conductivity can be maintained for a long time in a charge- discharge cycle, by using a composite grain, in which a coating layer made of a cobalt compound with a specific valence is formed on the surface of a nickel hydroxide grain possessing a specific physical properly, as an active material.

SOLUTION: In a composite grain constituting the powder used as an active material, a coating layer made of a cobalt compound, whose mean valence is more than 2 and not more than 3, is formed on the surface of a nickel hydroxide grain with a half value width of 0.35-0.7 degree for an X-ray diffraction peak on a grating face 101. For the cobalt compound whose mean valence is more than 2 and not more than 3, a mixture of cobalt hydroxide and cobalt oxyhydroxide or cobalt oxyhydroxide is available. A ratio of cobalt to the composite grain is 1-10% by weight desirably.

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CLAIMS

[Claim(s)]
[Claim 1] The paste type nickel pole for alkaline batteries which uses as an active material the powder which consists of a complex particle by which the average valence of cobalt comes to form from 2 the enveloping layer which consists of size and three or less cobalt compound in the front face of a nickel hydroxide particle whose half peak width of the X diffraction peak of a lattice plane (101) side is 0.35 – 0.7 degrees.
[Claim 2] The paste type nickel pole for alkaline batteries according to claim 1 said whose cobalt compound is the mixture or oxy-cobalt hydroxide of cobalt hydroxide and oxy-cobalt hydroxide.
[Claim 3] The paste type nickel pole for alkaline batteries according to claim 1 whose average valences of the cobalt of said cobalt compound are 2.5-2.93 especially.
[Claim 4] The paste type nickel pole for alkaline batteries according to claim 1 whose weight ratio to said complex particle of the cobalt in said enveloping layer is 1 – 10%.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to amelioration of the active material aiming at offering
in detail the paste type nickel pole which can hold high conductivity over the long period of time of a
charge-and-discharge cycle with respect to the paste type nickel pole for alkaline batteries.
[0002]
[Description of the Prior Art] Conventionally, the sintering type nickel pole which makes an active
material (nickel hydroxide) come to sink into the sintered carrier which the pierced steel plank etc.
was made to sinter nickel powder, and obtained it as a nickel pole for alkaline batteries is known
well.
[0003] In order to enlarge pack density of an active material on a sintering type nickel pole, it is
necessary to use a sintered carrier with large porosity. However, if association between the nickel
particles by sintering is weak and the porosity of a sintered carrier is enlarged, nickel powder will
dedrop come to be easy of association from a sintered carrier. Therefore, practically, the porosity of
a sintered carrier cannot be made larger than 80%, but, so, there is a problem that the pack density
of an active material is small in a sintering type nickel pole. Moreover, 10 micrometers or less and
since the aperture of the sintered compact of nickel powder is small, it also has the problem that
restoration to the substrate (sintered compact) of an active material must be performed by the
solution sinking-in method for repeating a complicated sinking-in process several times and
performing it.
[0004] Since it is such, the paste type nickel pole is proposed recently. A paste type nickel pole is
produced by filling up substrates with large porosity (foaming metal etc.) with the kneading object
(paste) of an active material (nickel hydroxide) and binder solutions (methyl cellulose water solution
etc.) directly. On the paste type nickel pole, since a substrate with large porosity can be used
(porosity can use 95% or more of substrate on the paste type nickel pole), while being able to
enlarge pack density of an active material, restoration to the substrate of an active material can be
performed once-like.
[0005] However, if a substrate with large porosity is used in order to enlarge pack density of an
active material on a paste type nickel pole, since the current collection capacity of a substrate will
worsen compared with a sintered carrier, conductivity worsens compared with a sintering type nickel
pole. This conductive badness causes the decline in an active material utilization factor, and the
ephemeralization of a charge-and-discharge cycle life.
[0006] Then, it is proposed that the average valence of cobalt, such as metal cobalt or cobalt
hydroxide, and 1 cobalt oxide, adds [the half peak width of the X diffraction peak of a lattice plane
(101) side] two or less cobalt compound to the nickel hydroxide powder (active material) of 0.8
degrees or more in order to improve the conductivity of this paste type nickel pole (JP,4-328257,A).

[0007] However, on this paste type nickel pole, since it was spread inside the particle and the conductivity of a plate fell while the cobalt which existed in the front face of a nickel hydroxide particle at the beginning piled up the charge-and-discharge cycle, it turned out that the sufficiently long alkaline battery of a charge-and-discharge cycle life is not obtained.

[0008] The place which this invention is made so that it may solve the above-mentioned problem which the conventional paste type nickel pole has, and is made into the purpose is to offer the paste type nickel pole for alkaline batteries which can maintain high conductivity over the long period of time of a charge-and-discharge cycle.

[0009]

[Means for Solving the Problem] The paste type nickel pole for alkaline batteries concerning this invention for attaining the above-mentioned purpose (this invention electrode) uses as an active material the powder which consists of a complex particle by which the average valence of cobalt comes to form the enveloping layer which consists of size and three or less cobalt compound from 2 in the front face of a nickel hydroxide particle whose half peak width of the X diffraction peak of a lattice plane (101) side is 0.35 - 0.7 degrees.

[0010] In this invention electrode, the nickel hydroxide particle whose half peak width of the X diffraction peak of a lattice plane (101) side is 0.35 - 0.7 degrees is used as a nickel hydroxide particle. While an active material utilization factor falls since the diffusion rate of the proton at the time of charge and discharge becomes small (when the crystallinity of a nickel hydroxide particle is too high) when the half peak width of the X diffraction peak of the lattice plane (101) side of a nickel hydroxide particle is less than 0.35 degrees, a charge-and-discharge cycle life becomes short. On the other hand, while the conductivity of the front face of a nickel hydroxide particle falls and an active material utilization factor falls as a result since diffusion inside [of the cobalt which covers the front face of a nickel hydroxide particle] a particle becomes easy to take place when this half peak width exceeds 0.7 degrees (when the crystallinity of a nickel hydroxide particle is too low), a charge-and-discharge cycle life becomes short.

[0011] In this invention electrode, size and three or less cobalt compound are used for the average valence of cobalt from 2 as a cobalt compound which covers a nickel hydroxide particle. When the average valence of cobalt is 2, the conductivity of a plate cannot fully be raised (when it is cobalt hydroxide). In addition, the average valence of cobalt is regulated by three or less because a cobalt compound with the larger average valence of cobalt than 3 does not exist. When raising an active material utilization factor, it is desirable that the average valence of cobalt covers with the cobalt compound of 2.5-2.93.

[0012] The nickel hydroxide particle whose half peak width of the X diffraction peak of a lattice plane (101) side is 0.35 - 0.7 degrees adds for example, a nickel-sulfate water solution and aqueous ammonia to the water in a reaction container, and is obtained as precipitate by carrying out predetermined time stirring mixing of the pH of liquid, after adding and adjusting an alkali water solution. A crystalline low nickel hydroxide particle is obtained greatly [the half peak width of the X diffraction peak of a lattice plane (101) side], so that pH of the liquid of reaction time is held highly. In addition, the solid-solution particle to which cobalt, zinc, cadmium, calcium, manganese, magnesium, etc. dissolved to the nickel hydroxide whose half peak width of the X diffraction peak of a lattice plane (101) side is 0.35 - 0.7 degrees is also contained in the nickel hydroxide particle in this invention.

[0013] After formation of an enveloping layer on a nickel hydroxide particle front face mixes for example, nickel hydroxide powder and cobalt hydroxide powder and adds an alkali water solution to this, it is performed by the approach of carrying out predetermined time heat-treatment at predetermined temperature. It may replace with cobalt hydroxide powder and 1 cobalt-oxide powder or metal cobalt powder may be used. The average valence of the cobalt of a cobalt compound can be adjusted to size and three or less range from 2 by adjusting the concentration, the heating processing time, or heat-treatment temperature of an alkali water solution. An enveloping layer with

the large average valence of cobalt is formed, so that the heating processing time is so long that heat-treatment temperature is so high that the concentration of an alkali water solution is high. An enveloping layer besides the above-mentioned approach can feed nickel hydroxide powder into a cobalt salt water solution, can add alkali, and can form it in the front face of a nickel hydroxide particle also by the approach of depositing cobalt hydroxide.

[0014] As size and three or less cobalt compound, the various mixture and the oxy-cobalt hydroxide of a rate of cobalt hydroxide (the valence of cobalt: 2) and oxy-cobalt hydroxide (the valence of cobalt: 3) are mentioned for the average valence of cobalt from 2.

[0015] 1 – 10% of the weight ratio to the complex particle of the cobalt in an enveloping layer is desirable. It is because the amount of the nickel hydroxide related to cell capacity decreases directly when cell capacity decreases and this weight ratio exceeds 10% on the other hand, while an active material utilization factor becomes low since conductivity is not enough when this weight ratio is less than 1%, so cell capacity decreases.

[0016] Since this invention electrode uses as an active material the complex particle which it comes to cover with the cobalt compound (for the average valence of cobalt to be size and three or less cobalt compound from 2) which has the conductivity which was excellent in the front face of the nickel hydroxide particle (nickel hydroxide particle whose half peak width of the X diffraction peak of a lattice plane (101) side is 0.35 – 0.7 degrees) which has moderate crystallinity, the conductivity which was excellent in the early stages of a charge-and-discharge cycle is maintained over a long period of time.

[0017]

[Embodiment of the Invention] This invention is widely applicable to the paste type nickel pole used as a positive electrode of alkaline batteries, such as a nickel cadmium battery and a nickel-hydrogen battery.

[0018]

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0019] (Examples 1-4)

[Production of nickel hydroxide powder] After the sodium-hydroxide water solution adjusted pH of liquid to 10.5, 11.0, 11.25, or 11.5 20% of the weight, adding and stirring in the water which held 0.1l. of aqueous ammonia to 35-degreeC in a tank 5% of the weight with 1l. of nickel-sulfate water solutions 30% of the weight, stirring was continued for 1 hour. The monitor of pH at this time was performed in the glass electrode pH meter with automatic temperature compensation. Subsequently, generated precipitate was carried out the ** exception, was rinsed, carried out the vacuum drying, and four sorts of nickel hydroxide powder was obtained. Subsequently, when asked for the half peak width of the X diffraction peak of the lattice plane (101) side of each nickel hydroxide powder from the X diffraction Fig. by the X diffraction of the following conditions, they were 0.35 degrees (pH10.5), 0.5 degrees (pH11.0), 0.6 degrees (pH11.25), and 0.7 degrees (pH11.5) in order.

[0020] <Conditions of an X diffraction> Anticathode Cu filter nickel tube voltage 40kV scan speed It is the tube electric current by 2.00-degree/. 100mA divergent slit 1 degree [0021] [Production of complex particle powder] The sodium-hydroxide water-solution 50 weight section was added 40% of the weight, after carrying out heating maintenance for 48 minutes, the vacuum drying of this was rinsed and carried out to 80-degreeC, the enveloping layer which consists of a cobalt compound on the particle front face of each nickel hydroxide powder was formed in the mixed powder of each above-mentioned nickel hydroxide powder 92 weight section and the cobalt hydroxide powder 8 weight section, and complex particle powder was produced to it.

[0022] Subsequently, all were 2.93 when asked by the approach of showing the average valence of the cobalt of the enveloping layer (cobalt compound) of each above-mentioned complex particle powder below.

[0023] <How to ask for the average valence of cobalt> Constant-rate **** of the sample is carried out, it melts to concentrated hydrochloric acid and the quantum of the amount of cobalt in a solution is carried out with an atomic absorption method. The amount of cobalt by which a quantum is carried out at this time is the total amount A of cobalt (total amount of divalent cobalt and trivalent cobalt) contained in an enveloping layer. next, the same as the point in the separately same sample — it *****, and melts to concentrated nitric acid, and a solution is filtered. Since trivalent cobalt does not melt into a nitric acid, the filtrate which contains only divalent cobalt by filtration is obtained. The quantum of the amount of cobalt in this filtrate is carried out with an atomic absorption method. The amount of cobalt by which a quantum is carried out at this time is the amount B of the divalent cobalt contained in an enveloping layer. The average valence of the cobalt of each sample is computed from a bottom type.

[0024] The average valence of cobalt = 3-B/A [0025] [Production of a paste type nickel pole] Each above-mentioned complex particle powder 100 weight section and the 1-% of the weight methyl cellulose water-solution 20 weight section were kneaded, the paste was prepared, the porous body (substrate) which consists of foaming metal (95% of porosity, 200 micrometers of average apertures) which carried out nickel plating of this paste was filled up, it dried, and it fabricated and the paste type nickel pole was produced.

[0026] [Production of an alkaline battery] Compared with each above-mentioned paste type nickel pole (positive electrode) and a positive electrode, electrochemical capacity produced the alkaline battery (cell capacity: about 700 mAh(s)) A1 of AA size - A4 using a well-known large paste type cadmium pole (negative electrode), the polyamide nonwoven fabric (separator), the 30-% of the weight potassium-hydroxide water solution (alkali electrolytic solution), the metal cell can, the metal cell lid, etc.

[0027] (Example 1 of a comparison) When producing nickel hydroxide powder, complex particle powder was produced like examples 1-4 except having held pH of liquid to 10. The half peak width of the lattice plane (101) side of nickel hydroxide powder was 0.30. Subsequently, the alkaline battery B1 of AA size was produced like examples 1-4 except having used this complex particle powder as positive active material.

[0028] (Example 2 of a comparison) When producing nickel hydroxide powder, complex particle powder was produced like examples 1-4 except having held pH of liquid to 12. The half peak width of the lattice plane (101) side of nickel hydroxide powder was 0.80. Subsequently, alkaline battery B-2 of AA size was produced like examples 1-4 except having used this complex particle powder as positive active material.

[0029] (Examples 3-9 of a comparison) the half peak width of the X diffraction peak of the lattice plane (101) side produced like examples 1-4 — 0.35, 0.5, 0.6, and 0. — 7 and 0.8 (pH12 at the time of production) — Each 0.9 (pH12.5 at the time of production), or 1.0 (pH13 at the time of production) nickel hydroxide powder 93.6 weight sections, Knead the 1 cobalt-oxide powder 6.4 weight section and the 1-% of the weight methyl cellulose water-solution 20 weight section, and a paste is prepared. The porous body (substrate) which consists of foaming metal (95% of porosity, 200 micrometers of average apertures) which carried out nickel plating was filled up with this paste, it dried, and it fabricated and the paste type nickel pole was produced. The alkaline batteries B3-B9 of AA size were produced like examples 1-4 except having used each of these paste type nickel poles as a positive electrode. In addition, cells B7-B9 are the conventional cells of the indication to JP,4-328257,A.

[0030] <The active material utilization factor of the paste type nickel pole used for each cell and charge-and-discharge cycle life of each cell> about each cell produced in examples 1-4 and the examples 1-9 of a comparison After charging 160% by 0.1C in 25-degreeC, the charge-and-discharge cycle trial which makes 1 cycle the process which discharges to 1.0V by 1C in 25-degreeC was performed, and the active material utilization factor of 10 cycle eye of the paste type nickel pole used for each cell and the charge-and-discharge cycle life of each cell were searched

for. The active material utilization factor was computed based on the bottom type.

[0031] Discharge capacity (mAh)/of an active material utilization factor (%) ={10 cycle eye ((amount g) of nickel hydroxide x288(mAh/g)}x100[0032]) Moreover, the number of charge-and-discharge cycles (time) until discharge capacity turns into 80% of the discharge capacity of 10 cycle eye estimated the charge-and-discharge cycle life. The active material utilization factor of 10 cycle eye of the paste type nickel pole used for each cell and the charge-and-discharge cycle life of each cell are shown in Table 1. The characteristic when setting to 100 the active material utilization factor of 10 cycle eye of the paste type nickel pole used for the cell A2 has shown the active material utilization factor. Moreover, the average valence of weight (%) and the ratio to the complex particle of the cobalt in an enveloping layer, and the cobalt of a cobalt compound and the half peak width (degree) of a nickel hydroxide particle are also shown in Table 1.

[0033]

[Table 1]

	コバルトの重量比率（％）	コバルトの平均価数	水酸化ニッケル粒子の半価幅（度）	１０サイクル目の活物質利用率（％）	充放電サイクル寿命（回）
電池A1	5	2.93	0.35	99	240
電池A2	5	2.93	0.5	100	250
電池A3	5	2.93	0.6	100	250
電池A4	5	2.93	0.7	99	230
電池B1	5	2.93	0.30	98	90
電池B2	5	2.93	0.80	98	100
電池B3	——	2	0.35	88	180
電池B4	——	2	0.5	89	190
電池B5	——	2	0.6	89	200
電池B6	——	2	0.7	88	190
電池B7	——	2	0.8	94	210
電池B8	——	2	0.9	95	210
電池B9	——	2	1.0	95	210

[0034] As shown in Table 1, a cell A1 - A4 have the high active material utilization factor of a paste type nickel pole, and although the active material utilization factor of a paste type nickel pole is high, a charge-and-discharge cycle life is short [the cell B1 by which the half peak width of the X diffraction peak of the lattice plane (101) side of a nickel hydroxide particle separates from the regulation range of this invention to a thing with a long charge-and-discharge cycle life and B-2 / a utilization factor]. In order to obtain an alkaline battery with a long charge-and-discharge cycle life from this fact highly [the active material utilization factor of a positive electrode], it turns out that it is necessary to use that whose half peak width of the X diffraction peak of a lattice plane (101) side is 0.35 - 0.7 degrees as a nickel hydroxide particle. In addition, compared with the cell B3 this half peak width of whose the half peak width of a nickel hydroxide particle is 0.35 - 0.7 degrees - B6, the active material utilization factor of a paste type nickel pole is high, although the cells B7-B9 of 0.8 degrees or more have a long charge-and-discharge cycle life, compared with a cell A1 - A4, its active material utilization factor of a paste type nickel pole is low, and a charge-and-discharge cycle life is short [the cells].

[0035] [The average valence of the cobalt of a cobalt compound and relation of an active material

utilization factor] The half peak width of the X diffraction peak of the lattice plane (101) side produced like the example 2 on the front face of the nickel hydroxide particle of 0.5 It is made to be the same as that of an example 2 except having changed the heating processing time at the time of forming an enveloping layer in 2 – 55 minutes. The enveloping layer to which the average valence of cobalt becomes order from the cobalt compound of 2.0, 2.1, 2.2, 2.3, 2.4, 2.45, 2.5, 2.6, 2.7, 2.8, 2.9, 2.93, and 3.0 is formed. 13 sorts of complex particle powder was produced (each weight ratio to the complex particle of the cobalt contained in each enveloping layer is 5%). Subsequently, each complex particle powder was used as an active material of a paste type nickel pole, and the alkaline battery of AA size was produced.

[0036] About each above-mentioned cell, the charge-and-discharge cycle trial of the same conditions as the point was performed, and the active material utilization factor of 10 cycle eye of the paste type nickel pole used for each cell was searched for. A result is shown in drawing 1 . Drawing 1 is the graph which the active material utilization factor was taken along the axis of ordinate, it took the average valence of cobalt along the axis of abscissa, respectively, and showed the average valence of the cobalt of a cobalt compound, and the relation of an active material utilization factor. The characteristic when the average valence of cobalt sets the active material utilization factor of 10 cycle eye of the paste type nickel pole of 2.7 to 100 has shown the active material utilization factor of an axis of ordinate.

[0037] As shown in drawing 1 , compared with the cell of 2, the active material utilization factor of a paste type nickel pole has [the cell with the larger average valence of cobalt than 2] the markedly high average valence of cobalt. In order to obtain the paste type nickel pole where an active material utilization factor is high from this fact, it turns out that it is necessary to use the complex particle which covered and obtained the nickel hydroxide particle with the cobalt compound with the larger average valence of cobalt than 2. Moreover, it turns out that it is desirable to use the complex particle powder from which the average valence of cobalt covered and obtained the nickel hydroxide particle with the cobalt compound of 2.5-2.93 from drawing 1 .

[0038] [Relation between the weight ratio to the complex particle of the cobalt in an enveloping layer, an active material utilization factor, and cell capacity] It is made to be the same as that of an example 2. It is made to be the same as that of an example 2 except having changed the amount of the cobalt hydroxide used at the time of the half peak width of the X diffraction peak of the produced lattice plane (101) side forming an enveloping layer in the front face of the nickel hydroxide particle of 0.5. The enveloping layer of the various thickness which the average valence of cobalt becomes from the cobalt compound of 2.93 was formed, and the weight ratio to said complex particle of the cobalt in an enveloping layer produced six sorts of different complex particle powder from 0.5%, 1%, 5%, 7.5%, 10%, and 11%. Subsequently, each complex particle powder was used as an active material, and the alkaline battery of a paste type nickel pole and AA size was produced.

[0039] About each above-mentioned cell, the charge-and-discharge cycle trial of the same conditions as the point was performed, and the active material utilization factor of 10 cycle eye of the paste type nickel pole used for each cell and the cell capacity of 10 cycle eye of each cell were calculated. A result is shown in drawing 2 and drawing 3 , respectively. Drawing 2 is the graph which took the active material utilization factor along the axis of ordinate, took the weight ratio (%) along the axis of abscissa, respectively, and showed the relation between the weight ratio to the complex particle of the cobalt in an enveloping layer, and an active material utilization factor, and drawing 3 is the graph which the active material utilization factor (%) was taken along the axis of ordinate, it took cell capacity along the axis of abscissa, respectively, and showed the relation between the above-mentioned weight ratio and cell capacity. In addition, the characteristic when setting to 100 the active material utilization factor and cell capacity of 10 cycle eye of a cell whose weight ratio to the complex particle of cobalt is 5%, respectively has shown the active material utilization factor of the axis of ordinate of drawing 2 , and the cell capacity of the axis of ordinate of drawing 3 .

[0040] Drawing 2 shows that what has a high active material utilization factor is obtained, when the

weight ratio to the complex particle of the cobalt in an enveloping layer is 1% or more. Moreover, drawing 3 shows that what has a big cell capacity is obtained, when the weight ratio to the complex particle of the cobalt in an enveloping layer is 1 – 10%. It turns out that it is desirable to form an enveloping layer so that the weight ratio to the complex particle of the cobalt in an enveloping layer may become the range which is 1 – 10% from these results.
[0041]
[Effect of the Invention] It becomes possible [this invention electrode], since the conductivity which was excellent in the early stages of a charge–and–discharge cycle is maintained over a long period of time to obtain an alkaline battery with a long charge–and–discharge cycle life with the high active material utilization factor of a positive electrode by using this as a positive electrode.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the graph which shows the average valence of the cobalt of a cobalt compound, and the relation of an active material utilization factor.
[Drawing 2] It is the graph which shows the relation between the weight ratio to the complex particle of the cobalt in an enveloping layer, and an active material utilization factor.
[Drawing 3] It is the graph which shows the relation between the weight ratio to the complex particle of the cobalt in an enveloping layer, and cell capacity.

[Translation done.]

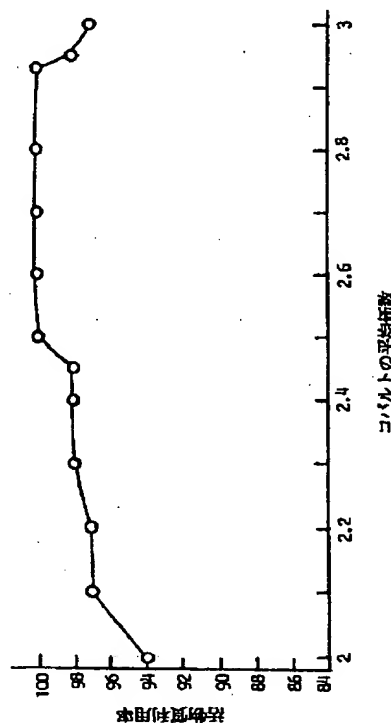| (51)Int.Cl.^{6}		識別記号	庁内整理番号	FI		技術表示箇所
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審査請求　未請求　請求項の数4　FD　（全 7 頁）

(54)【発明の名称】　アルカリ蓄電池用のペースト式ニッケル極

(57)【要約】

【解決手段】格子面（101）面のX線回折ピークの半価幅が0.35～0.7度の水酸化ニッケル粒子の表面に、コバルトの平均価数が2より大、且つ3以下のコバルト化合物からなる被覆層を形成してなる複合体粒子からなる粉末が活物質として用いられている。

【効果】本発明電極は、充放電サイクル初期の優れた導電性が長期にわたって維持されるので、これを正極として用いることにより、正極の活物質利用率が高い、充放電サイクル寿命の長いアルカリ蓄電池を得ることが可能となる。

【特許請求の範囲】
【請求項1】格子面（１０１）面のＸ線回折ピークの半価幅が０．３５〜０．７度の水酸化ニッケル粒子の表面に、コバルトの平均価数が２より大、且つ３以下のコバルト化合物からなる被覆層を形成してなる複合体粒子からなる粉末を活物質とするアルカリ蓄電池用のペースト式ニッケル極。
【請求項2】前記コバルト化合物が、水酸化コバルトとオキシ水酸化コバルトとの混合物又はオキシ水酸化コバルトである請求項1記載のアルカリ蓄電池用のペースト式ニッケル極。
【請求項3】前記コバルト化合物のコバルトの平均価数が、特に、２．５〜２．９３である請求項1記載のアルカリ蓄電池用のペースト式ニッケル極。
【請求項4】前記被覆層中のコバルトの前記複合体粒子に対する重量比率が、１〜１０％である請求項1記載のアルカリ蓄電池用のペースト式ニッケル極。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、アルカリ蓄電池用のペースト式ニッケル極に係わり、詳しくは、充放電サイクルの長期にわたって高い導電性を保持し得るペースト式ニッケル極を提供することを目的とした、活物質の改良に関する。
【０００２】
【従来の技術及び発明が解決しようとする課題】従来、アルカリ蓄電池用のニッケル極としては、ニッケル粉末を穿孔鋼板等に焼結させて得た焼結基板に活物質（水酸化ニッケル）を含浸させてなる焼結式ニッケル極がよく知られている。
【０００３】焼結式ニッケル極において活物質の充填密度を大きくするためには、多孔度の大きい焼結基板を用いる必要がある。しかし、焼結によるニッケル粒子間の結合は弱く、焼結基板の多孔度を大きくするとニッケル粉末が焼結基板から脱落し易くなる。従って、実用上は、焼結基板の多孔度を８０％より大きくすることができず、それゆえ焼結式ニッケル極には、活物質の充填密度が小さいという問題がある。また、ニッケル粉末の焼結体の孔径は１０μm以下と小さいため、活物質の基板（焼結体）への充填を、煩雑な含浸工程を数回繰り返し行う必要がある溶液含浸法により行わなければならないという問題もある。
【０００４】このようなことから、最近、ペースト式ニッケル極が提案されている。ペースト式ニッケル極は、活物質（水酸化ニッケル）と結合剤溶液（メチルセルロース水溶液など）との混練物（ペースト）を多孔度の大きい基板（発泡メタルなど）に直接充填することにより作製される。ペースト式ニッケル極では、多孔度の大きい基板を用いることができるので（ペースト式ニッケル極では多孔度が９５％以上の基板を用いることができ

る）、活物質の充填密度を大きくすることができるとともに、活物質の基板への充填を一回的に行うことができる。
【０００５】しかしながら、ペースト式ニッケル極において活物質の充填密度を大きくするべく多孔度の大きい基板を用いると、基板の集電能力が焼結基板に比べて悪くなるので、焼結式ニッケル極に比べて、導電性が悪くなる。斯かる導電性の悪さは、活物質利用率の低下及び充放電サイクル寿命の短命化を招く。
【０００６】そこで、斯かるペースト式ニッケル極の導電性を改良するべく、格子面（１０１）面のＸ線回折ピークの半価幅が０．８度以上の水酸化ニッケル粉末（活物質）に、金属コバルト、又は、水酸化コバルト、一酸化コバルト等のコバルトの平均価数が２以下のコバルト化合物を添加することが提案されている（特開平4−328257号）。
【０００７】しかしながら、このペースト式ニッケル極では、当初水酸化ニッケル粒子の表面に存在していたコバルトが充放電サイクルを重ねるうちに粒子内部に拡散して、極板の導電性が低下してしまうので、充放電サイクル寿命の充分長いアルカリ蓄電池は得られないことが分かった。
【０００８】本発明は、従来のペースト式ニッケル極が有する上述の問題を解決するべくなされたものであって、その目的とするところは、充放電サイクルの長期にわたって高い導電性を維持することができる、アルカリ蓄電池用のペースト式ニッケル極を提供するにある。
【０００９】
【課題を解決するための手段】上記目的を達成するための本発明に係るアルカリ蓄電池用のペースト式ニッケル極（本発明電極）は、格子面（１０１）面のＸ線回折ピークの半価幅が０．３５〜０．７度の水酸化ニッケル粒子の表面に、コバルトの平均価数が２より大、且つ３以下のコバルト化合物からなる被覆層を形成してなる複合体粒子からなる粉末を活物質とする。
【００１０】本発明電極においては、水酸化ニッケル粒子として、格子面（１０１）面のＸ線回折ピークの半価幅が０．３５〜０．７度の水酸化ニッケル粒子が用いられる。水酸化ニッケル粒子の格子面（１０１）面のＸ線回折ピークの半価幅が０．３５度未満の場合（水酸化ニッケル粒子の結晶性が高すぎる場合）は、充放電時のプロトンの拡散速度が小さくなるので、活物質利用率が低下するとともに、充放電サイクル寿命が短くなる。一方、同半価幅が０．７度を越えた場合（水酸化ニッケル粒子の結晶性が低すぎる場合）は、水酸化ニッケル粒子の表面を被覆するコバルトの粒子内部への拡散が起こり易くなるので、水酸化ニッケル粒子の表面の導電性が低下し、その結果活物質利用率が低下するとともに、充放電サイクル寿命が短くなる。
【００１１】本発明電極においては、水酸化ニッケル粒

子を被覆するコバルト化合物として、コバルトの平均価数が2より大、且つ3以下のコバルト化合物が用いられる。コバルトの平均価数が2の場合（水酸化コバルトの場合）は、充分に極板の導電性を高めることができない。なお、コバルトの平均価数が3以下に規制されるのは、コバルトの平均価数が3より大きいコバルト化合物が存在しないからである。活物質利用率を高める上で、コバルトの平均価数が2．5～2．93のコバルト化合物で被覆することが好ましい。

【0012】格子面（101）面のX線回折ピークの半価幅が0．35～0．7度の水酸化ニッケル粒子は、例えば、硫酸ニッケル水溶液と、アンモニア水とを反応容器内の水に加え、液のpHをアルカリ水溶液を添加して調整した後、所定時間攪拌混合することにより沈殿物として得られる。反応時の液のpHを高く保持するほど、格子面（101）面のX線回折ピークの半価幅が大きい、すなわち結晶性の低い水酸化ニッケル粒子が得られる。なお、本発明における水酸化ニッケル粒子には、格子面（101）面のX線回折ピークの半価幅が0．35～0．7度の水酸化ニッケルに、コバルト、亜鉛、カドミウム、カルシウム、マンガン、マグネシウムなどが固溶した固溶体粒子も含まれる。

【0013】水酸化ニッケル粒子表面への被覆層の形成は、例えば水酸化ニッケル粉末と水酸化コバルト粉末とを混合し、これにアルカリ水溶液を添加した後、所定温度で、所定時間加熱処理する方法により行われる。水酸化コバルト粉末に代えて、一酸化コバルト粉末又は金属コバルト粉末を用いてもよい。アルカリ水溶液の濃度、加熱処理時間又は加熱処理温度を調節することにより、コバルト化合物のコバルトの平均価数を2より大、且つ3以下の範囲に調整することができる。アルカリ水溶液の濃度が高いほど、加熱処理温度が高いほど、また加熱処理時間が長いほど、コバルトの平均価数が大きい被覆層が形成される。上記の方法の他、被覆層は、水酸化ニッケル粉末をコバルト塩水溶液に投入し、アルカリを添加して、水酸化ニッケル粒子の表面に水酸化コバルトを析出させる方法によっても形成することができる。

【0014】コバルトの平均価数が2より大、且つ3以下のコバルト化合物としては、水酸化コバルト（コバルトの価数：2）とオキシ水酸化コバルト（コバルトの価数：3）との種々の割合の混合物及びオキシ水酸化コバルトが挙げられる。

【0015】被覆層中のコバルトの複合体粒子に対する重量比率は、1～10％が好ましい。この重量比率が1％未満の場合は、導電性が充分でないために、活物質利用率が低くなるとともに、電池容量が減少し、一方この重量比率が10％を超えた場合は、電池容量に直接関係する水酸化ニッケルの量が少なくなるため、電池容量が減少するからである。

【0016】本発明電極は、適度の結晶性を有する水酸化ニッケル粒子（格子面（101）面のX線回折ピークの半価幅が0．35～0．7度の水酸化ニッケル粒子）の表面を、優れた導電性を有するコバルト化合物（コバルトの平均価数が2より大、且つ3以下のコバルト化合物）で被覆してなる複合体粒子を活物質とするので、充放電サイクル初期の優れた導電性が長期にわたって維持される。

【0017】
【発明の実施の形態】本発明は、ニッケルーカドミウム蓄電池、ニッケルー水素蓄電池などのアルカリ蓄電池の正極として使用されるペースト式ニッケル極に、広く適用可能である。

【0018】
【実施例】以下、本発明を実施例に基づいてさらに詳細に説明するが、本発明は下記実施例に何ら限定されるものではなく、その要旨を変更しない範囲において適宜変更して実施することが可能なものである。

【0019】（実施例1～4）
〔水酸化ニッケル粉末の作製〕30重量％硫酸ニッケル水溶液1リットルと、5重量％アンモニア水0．1リットルとを、水槽中の35℃に保持した水に添加し、攪拌しながら20重量％水酸化ナトリウム水溶液にて液のpHを10．5、11．0、11．25又は11．5に調整した後、1時間攪拌を続けた。このときのpHの監視は自動温度補償付きガラス電極pHメータにて行った。次いで、生成した沈殿物をろ別し、水洗し、真空乾燥して、4種の水酸化ニッケル粉末を得た。次いで、各水酸化ニッケル粉末の格子面（101）面のX線回折ピークの半価幅を、下記の条件のX線回折によるX線回折図より求めたところ、順に0．35度（pH10．5）、0．5度（pH11．0）、0．6度（pH11．25）、0．7度（pH11．5）であった。

【0020】（X線回折の条件）
対陰極　　　Cu
フィルタ　　Ni
管電圧　　　40kV
走査速度　　2．00°／分
管電流　　　100mA
発散スリット　1°

【0021】〔複合体粒子粉末の作製〕上記の各水酸化ニッケル粉末92重量部と水酸化コバルト粉末8重量部との混合粉末に、40重量％水酸化ナトリウム水溶液50重量部を添加し、これを80℃に48分間加熱保持した後、水洗し、真空乾燥して、各水酸化ニッケル粉末の粒子表面にコバルト化合物からなる被覆層を形成して、複合体粒子粉末を作製した。

【0022】次いで、上記の各複合体粒子粉末の被覆層（コバルト化合物）のコバルトの平均価数を下記に示す方法により求めたところ、いずれも2．93であった。

【0023】（コバルトの平均価数の求め方）試料を一

定量秤取し、濃塩酸に溶かし、溶液中のコバルト量を原子吸光法にて定量する。このとき定量されるコバルト量は被覆層中に含まれる全コバルト量（2価コバルト及び3価コバルトの総量）Aである。次に、別途同じ試料を先と同じ量秤取し、濃硝酸に溶かし、溶液をろ過する。3価コバルトは硝酸に溶けないため、ろ過により2価コバルトのみを含むろ液が得られる。このろ液中のコバルト量を原子吸光法にて定量する。このとき定量されるコバルト量は被覆層中に含まれる2価コバルトの量Bである。各試料のコバルトの平均価数を下式より算出する。

【0024】コバルトの平均価数＝3−B／A

【0025】〔ペースト式ニッケル極の作製〕上記の各複合体粒子粉末100重量部と、1重量％メチルセルロース水溶液20重量部とを混練してペーストを調製し、このペーストをニッケルめっきした発泡メタル（多孔度95％、平均孔径200μm）からなる多孔体（基板）に充填し、乾燥し、成形して、ペースト式ニッケル極を作製した。

【0026】〔アルカリ蓄電池の作製〕上記の各ペースト式ニッケル極（正極）、正極に比べて電気化学的容量が大きい公知のペースト式カドミウム極（負極）、ポリアミド不織布（セパレータ）、30重量％水酸化カリウム水溶液（アルカリ電解液）、金属製の電池缶、金属製の電池蓋などを用いて、AAサイズのアルカリ蓄電池（電池容量：約700mAh）A1〜A4を作製した。

【0027】（比較例1）水酸化ニッケル粉末を作製する際に液のpHを10に保持したこと以外は実施例1〜4と同様にして、複合体粒子粉末を作製した。水酸化ニッケル粉末の格子面（101）面の半価幅は0．30であった。次いで、この複合体粒子粉末を正極活物質として用いたこと以外は実施例1〜4と同様にして、AAサイズのアルカリ蓄電池B1を作製した。

【0028】（比較例2）水酸化ニッケル粉末を作製する際に液のpHを12に保持したこと以外は実施例1〜4と同様にして、複合体粒子粉末を作製した。水酸化ニッケル粉末の格子面（101）面の半価幅は0．80であった。次いで、この複合体粒子粉末を正極活物質として用いたこと以外は実施例1〜4と同様にして、AAサイズのアルカリ蓄電池B2を作製した。

【0029】（比較例3〜9）実施例1〜4と同様にして作製した格子面（101）面のX線回折ピークの半価幅が0．35、0．5、0．6、0．7、0．8（作製時のpH12）、0．9（作製時のpH12．5）、1．0（作製時のpH13）の各水酸化ニッケル粉末93．6重量部と、一酸化コバルト粉末6．4重量部と、1重量％メチルセルロース水溶液20重量部とを混練してペーストを調製し、このペーストをニッケルめっきした発泡メタル（多孔度95％、平均孔径200μm）からなる多孔体（基板）に充填し、乾燥し、成形して、ペースト式ニッケル極を作製した。これらの各ペースト式ニッケル極を正極として用いたこと以外は実施例1〜4と同様にして、AAサイズのアルカリ蓄電池B3〜B9を作製した。なお、電池B7〜B9は特開平4−328257に開示の従来電池である。

【0030】〈各電池に使用したペースト式ニッケル極の活物質利用率及び各電池の充放電サイクル寿命〉実施例1〜4及び比較例1〜9で作製した各電池について、25℃にて0．1Cで160％充電した後、25℃にて1Cで1．0Vまで放電する工程を1サイクルとする充放電サイクル試験を行い、各電池に使用したペースト式ニッケル極の10サイクル目の活物質利用率及び各電池の充放電サイクル寿命を求めた。活物質利用率は、下式に基づいて算出した。

【0031】活物質利用率（％）＝{10サイクル目の放電容量（mAh）／（水酸化ニッケル量（g）×288（mAh／g）}×100

【0032】また、充放電サイクル寿命は、放電容量が10サイクル目の放電容量の80％になるまでの充放電サイクル数（回）で評価した。各電池に使用したペースト式ニッケル極の10サイクル目の活物質利用率及び各電池の充放電サイクル寿命を表1に示す。活物質利用率は、電池A2に使用したペースト式ニッケル極の10サイクル目の活物質利用率を100としたときの指数で示してある。また、表1には、被覆層中のコバルトの複合体粒子に対する重量比率（％）、コバルト化合物のコバルトの平均価数及び水酸化ニッケル粒子の半価幅（度）も示してある。

【0033】

【表1】

	コバルトの重量比率（％）	コバルトの平均価数	水酸化ニッケル粒子の半価幅（度）	10サイクル目の活物質利用率（％）	充放電サイクル寿命（回）
電池A1	5	2.93	0.35	99	240
電池A2	5	2.93	0.35	100	250
電池A3	5	2.93	0.6	100	250
電池A4	5	2.93	0.7	99	230
電池B1	5	2.93	0.30	98	90
電池B2	5	2.93	0.8	98	100
電池B3	———	2	0.35	88	180
電池B4	———	2	0.5	89	190
電池B5	———	2	0.6	89	200
電池B6	———	2	0.7	88	190
電池B7	———	2	0.8	94	210
電池B8	———	2	0.9	95	210
電池B9	———	2	1.0	95	210

【0034】表1に示すように、電池A1〜A4は、ペースト式ニッケル極の活物質利用率が高く、充放電サイクル寿命が長いのに対して、水酸化ニッケル粒子の格子面（101）面のX線回折ピークの半価幅が本発明の規制範囲を外れる電池B1，B2は、ペースト式ニッケル極の活物質利用率は高いものの、充放電サイクル寿命が短い。この事実から、正極の活物質利用率が高く、且つ充放電サイクル寿命が長いアルカリ蓄電池を得るためには、水酸化ニッケル粒子として、格子面（101）面のX線回折ピークの半価幅が0.35〜0.7度のものを用いる必要があることが分かる。なお、水酸化ニッケル粒子の半価幅が0.8度以上の電池B7〜B9は、同半価幅が0.35〜0.7度の電池B3〜B6に比べて、ペースト式ニッケル極の活物質利用率が高く、充放電サイクル寿命が長いものの、電池A1〜A4に比べると、ペースト式ニッケル極の活物質利用率が低く、充放電サイクル寿命が短い。

【0035】〔コバルト化合物のコバルトの平均価数と活物質利用率の関係〕実施例2と同様にして作製した格子面（101）面のX線回折ピークの半価幅が0.5の水酸化ニッケル粒子の表面に、被覆層を形成する際の加熱処理時間を2〜55分の間で変えたこと以外は実施例2と同様にしてコバルトの平均価数が順に2.0、2.1、2.2、2.3、2.4、2.45、2.5、2.6、2.7、2.8、2.9、2.93、3.0のコバルト化合物からなる被覆層を形成して、13種の複合体粒子粉末を作製した（各被覆層中に含まれるコバルトの複合体粒子に対する重量比率は、いずれも5％である）。次いで、各複合体粒子粉末をペースト式ニッケル極の活物質として使用して、AAサイズのアルカリ蓄電

池を作製した。
【0036】上記の各電池について、先と同じ条件の充放電サイクル試験を行い、各電池に使用したペースト式ニッケル極の10サイクル目の活物質利用率を求めた。結果を図1に示す。図1は、コバルト化合物のコバルトの平均価数と活物質利用率の関係を、縦軸に活物質利用率を、横軸にコバルトの平均価数を、それぞれとって示したグラフである。縦軸の活物質利用率は、コバルトの平均価数が2.7のペースト式ニッケル極の10サイクル目の活物質利用率を100としたときの指数で示してある。

【0037】図1に示すように、コバルトの平均価数が2より大きい電池は、コバルトの平均価数が2の電池に比べて、ペースト式ニッケル極の活物質利用率が格段高い。この事実から、活物質利用率が高いペースト式ニッケル極を得るためには、コバルトの平均価数が2より大きいコバルト化合物で水酸化ニッケル粒子を被覆して得た複合体粒子を用いる必要があることが分かる。また、図1より、コバルトの平均価数が2.5〜2.93のコバルト化合物で水酸化ニッケル粒子を被覆して得た複合体粒子粉末を用いることが好ましいことが分かる。

【0038】〔被覆層中のコバルトの複合体粒子に対する重量比率と活物質利用率及び電池容量の関係〕実施例2と同様にして作製した格子面（101）面のX線回折ピークの半価幅が0.5の水酸化ニッケル粒子の表面に被覆層を形成する際の水酸化コバルトの使用量を変化させたこと以外は実施例2と同様にしてコバルトの平均価数が2.93のコバルト化合物からなる種々の厚みの被覆層を形成して、被覆層中のコバルトの前記複合体粒子に対する重量比率が0.5％、1％、5％、7.5％、

１０％、１１％と異なる６種の複合体粒子粉末を作製した。次いで、各複合体粒子粉末を活物質として使用して、ペースト式ニッケル極及びＡＡサイズのアルカリ蓄電池を作製した。

【００３９】上記の各電池について、先と同じ条件の充放電サイクル試験を行い、各電池に使用したペースト式ニッケル極の１０サイクル目の活物質利用率及び各電池の１０サイクル目の電池容量を求めた。結果を、それぞれ図２及び図３に示す。図２は、被覆層中のコバルトの複合体粒子に対する重量比率と活物質利用率の関係を、縦軸に活物質利用率を、横軸に重量比率（％）を、それぞれとって示したグラフであり、また図３は、上記重量比率と電池容量の関係を、縦軸に活物質利用率（％）を、横軸に電池容量を、それぞれとって示したグラフである。なお、図２の縦軸の活物質利用率及び図３の縦軸の電池容量は、それぞれコバルトの複合体粒子に対する重量比率が５％の電池の１０サイクル目の活物質利用率及び電池容量を１００としたときの指数で示してある。

【００４０】図２より、被覆層中のコバルトの複合体粒子に対する重量比率が１％以上の場合に、活物質利用率

が高いものが得られることが分かる。また、図３より、被覆層中のコバルトの複合体粒子に対する重量比率が１〜１０％の場合に、大きな電池容量を有するものが得られることが分かる。これらの結果から、被覆層中のコバルトの複合体粒子に対する重量比率が１〜１０％の範囲になるように、被覆層を形成することが好ましいことが分かる。

【００４１】

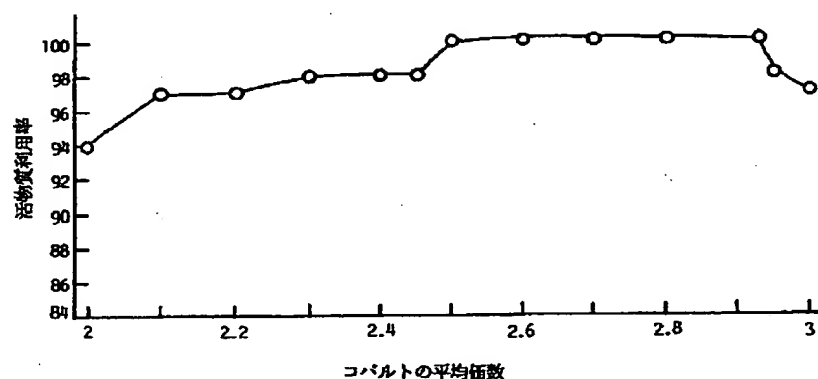【発明の効果】本発明電極は、充放電サイクル初期の優れた導電性が長期にわたって維持されるので、これを正極として用いることにより、正極の活物質利用率が高い、充放電サイクル寿命が長いアルカリ蓄電池を得ることが可能となる。

【図面の簡単な説明】
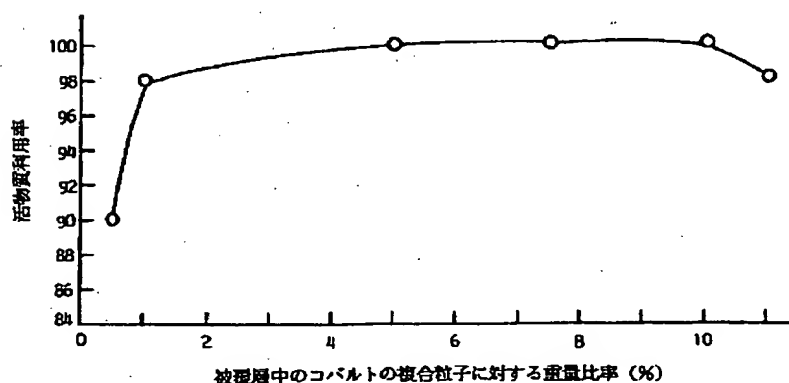
【図１】コバルト化合物のコバルトの平均価数と活物質利用率の関係を示すグラフである。

【図２】被覆層中のコバルトの複合体粒子に対する重量比率と活物質利用率の関係を示すグラフである。
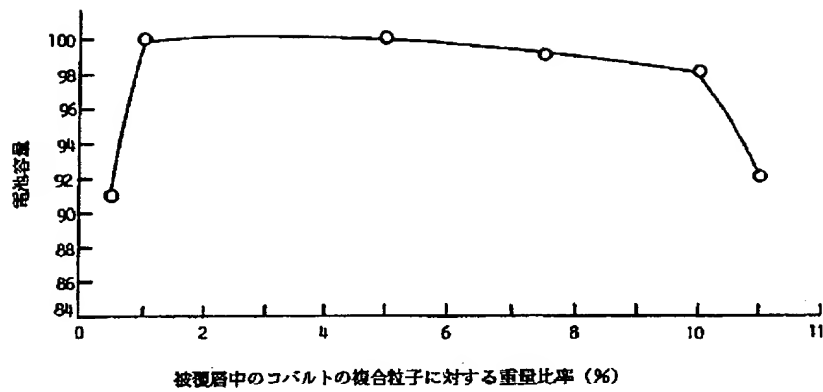
【図３】被覆層中のコバルトの複合体粒子に対する重量比率と電池容量の関係を示すグラフである。

【図１】

【図２】

【図3】

被覆層中のコバルトの複合粒子に対する重量比率（%）

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